

Report for 2002ID15B: Metal(loid) Release from Contaminated Sediments in Lake Coeur d'Alene, Idaho

- Water Resources Research Institute Reports:
 - NA
- Conference Proceedings:
 - NA
- Articles in Refereed Scientific Journals:
 - NA
- Dissertations:
 - NA
- Book Chapters:
 - NA
- Other Publications:
 - NA

Report Follows

Problem and Research Objectives:

Lake Coeur d'Alene (CDA) in Idaho is the second largest natural lake in the Inland Northwest. Lake CDA provides drinking water for at least five communities and serves as a primary recreational area for inhabitants of the Pacific Northwest. Over the last century Lake CDA became, and continues to be, the major collecting bed for contaminated sediments produced during mining and ore processing activities. As a result of these mining activities tailings enriched in Pb, Zn, As, Cd, and other trace elements were deposited in stream banks and bars along the South Fork and main stem of the Coeur d'Alene River. These materials have been regularly resuspended during periods of high stream flow and secondarily transported into Lake CDA. Our objectives are to 1) determine whether there is currently a significant flux of metal contaminants from the sediment of Lake CDA to the water column and 2) predict how anthropogenic alteration of lake trophic status will influence this flux. It has been assumed that eutrophication will promote trace element release (Woods, 1989). This prediction is based on the assumption that metals in the lake occur predominantly in their oxide and hydroxide forms, and that there is no anoxic metal binding mechanism. Thus one of the principal means of keeping toxic trace elements immobilized in lakebed sediments may be to carefully manage the lake nutrient status to avoid the development of anoxic conditions. Others have suggested that a large fraction of metal(loid) contaminants partition with a chemically refractory sulfidic phase (Harrington et al., 1998; 1999) and that these metal sulfides are inherently stable under reducing condition. The mechanisms responsible for metal retention and cycling remain uncertain, making accurate assessments of current flux and predictions of future environmental contamination difficult. Our proposed research is focused on resolving the controversy by directly determining the dominance of sulfidic phases in the sediments.

Methodology:

To determine S species in the lake sediment pore waters we are using several approaches, including cyclic voltammetry and chromatographic separation. However, these techniques are designed for analysis of the solution phase only. Harrington et al. (1998) used selective sequential extractions on sediments to determine the S-metalloid associations. These experiments are based on operationally defined S pools. Interpretation of geochemical cycling data will be greatly improved by using direct techniques to speciate sediment S. To speciate solid phase S we used X-ray absorption near edge spectroscopy (XANES). Sulfur has multiple oxidation states that have been observed to range from -2 to +6. XANES is ideally suited for determining oxidation state and in many cases can provide information about molecular speciation. Since the formation of S complexes and precipitates with the metal(loid) contaminants in the sediments is dependent on the oxidation state, the information obtained from XANES will be extremely valuable for this project.

Sample Collection and Handling. Sediment cores were collected by divers from the southern end of Lake CDA located in Northern Idaho on April 8, 2003. Three principle sites were chosen for detailed study, one site near the mouth of the uncontaminated St. Joe River to be used as a control and two sites near the mouth of the Coeur d'Alene River which transports the contaminated sediments from the Coeur d'Alene mining district to the lake. Divers collected 36-

cm cores in acid washed 4.7-cm diameter polycarbonate tubes. The divers capped the cores prior to bringing them to the surface where they were immediately sealed and placed upright in nitrogen-filled containers maintained at 4°C until delivered to the laboratory. Duplicate cores were taken at each site.

The cores were individually placed in an Innovative Technologies, Inc., Model SI nitrogen-filled glove box prior to extruding them from the polycarbonate cores. The cores were sectioned and representative samples were taken from 3 cm, 6 cm, 12 cm, 24 cm, 30 cm and 36 cm. Care was taken to eliminate sediment smearing between sampling depths. The representative samples were placed in acid washed and rinsed wide mouth 20-mL polypropylene vials. The vials were then placed in double zip lock bags prior to removing from the glove box and maintained on ice until XANES analysis was performed at Brookhaven, N.Y. Duplicate cores were sectioned for each site.

XANES Spectroscopy. Spectroscopic analysis was performed at the National Synchrotron Light Source (NSLS) in Brookhaven, NY. XANES data collection was done on beamline X-19A using a Si(111) crystal monochromator. This beamline is designed for collecting spectra from samples in the lower energy range (2100 - 8000 eV) and has a sample chamber environment that is appropriate for our materials. Sediment samples were mounted on filter paper and placed in the spectrometer. All analyses were performed under a He gas atmosphere. Each sample was scanned twice from 2372 to 2550 eV. The white-line peak maximum of sulfate was set at 2483.1 eV and used for reference.

Principle Findings and Significance:

XANES analysis was performed on duplicate cores of the three sites from Lake CDA; St. Joe, Peaceful Point, and Harlow Point. Prior research confirmed St. Joe can be used as the control site and Peaceful Point and Harlow Point can be used as the contaminated sites. Sulfur has multiple oxidation states that range from -2 to +6. Four sulfur oxidation states were identified and further identification of organic and inorganic sulfur was possible due to the distinct absorption edges of the inorganic sulfides. Sulfate, a sulfur species with an oxidation state of +6, decreases with depth at all sites as observed in Figs. 1-3. This is corroborated by the data analysis of pore water which indicates an increase in reducing conditions with depth (Fig. 4), an environment where oxidized forms of sulfur are unstable. Pyrite, an iron sulfide in which sulfur has an average oxidation state of -1, increases with depth at all sites as observed in Figs. 1-3. The increase in reducing conditions with depth also supports this finding. Pyrite was found in the near surface samples at all sites because it is a primary mineral found in the Coeur d'Alene mining district and is episodically transported to the lake during flood events. The remaining two species are organic forms of sulfur which would be unavailable to form complexes with contaminants. It would not be possible for inorganic sulfate to exist at the reducing conditions found with depth, which indicates that the sulfate remaining below the redox boundary is most likely in the form of an organic ester-bonded sulfate.

This project has resolved the disagreement between the findings of Horowitz (1992, 1999) and Harrington with respect to the oxidation status of the sediments. The near surface sediments exist

in an oxidizing environment as indicated by the presence of nitrate and sulfate in the pore water (Fig. 4). However within 2.5 cm the manganese (Mn) redox boundary exists as evidenced by the presence of Mn in the pore water. Within 5 cm of the (Mn) redox boundary the sulfate anion concentration is below the detection limit which would indicate sulfate reduction and concomitant production of the sulfide ion. The sulfide ion has significant binding capacities with metal contaminants. Further research is necessary to determine if the sulfide ion is present in an amount that significantly affects the mobility of the metal contaminants.

We have shown that metal contaminants in the top 2.5 cm of sediment are most likely associated with oxidized solid phases or reduced solid phase materials which are relatively stable in the presence of oxygen. Metals below 2.5 cm must be associated with reduced solid phase materials that include diagenetically produced pyrite. Metal associations with oxidized solid phase materials in the upper layer of the sediments will be altered if Lake CDA's trophic status shifts to a eutrophic state.

Literature Cited

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- Woods, P.F. 1989. Hypolimnetic concentrations of dissolved oxygen, nutrients and trace elements in Coeur d'Alene Lake, Idaho. U.S. Geological Survey. Water-Resources Investigations Report 89-4032.

Descriptors: heavy metals, mining, sediments, contaminant flux

Articles in Refereed Scientific Journals: NA

Book Chapters: NA

Dissertations: NA

Water Resources Research Institute Reports: NA

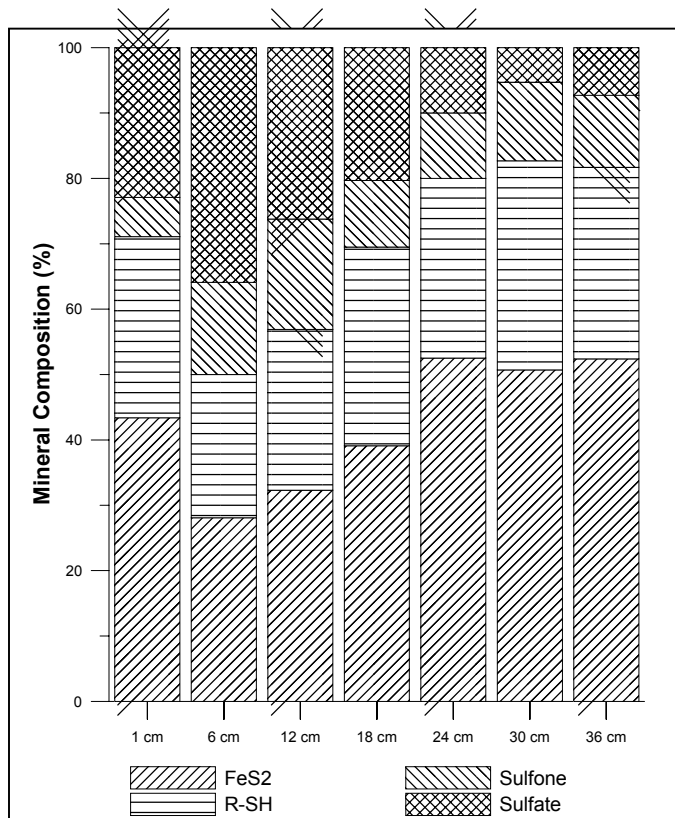


Figure 1: St Joe XANES spectra analysis by sediment depth

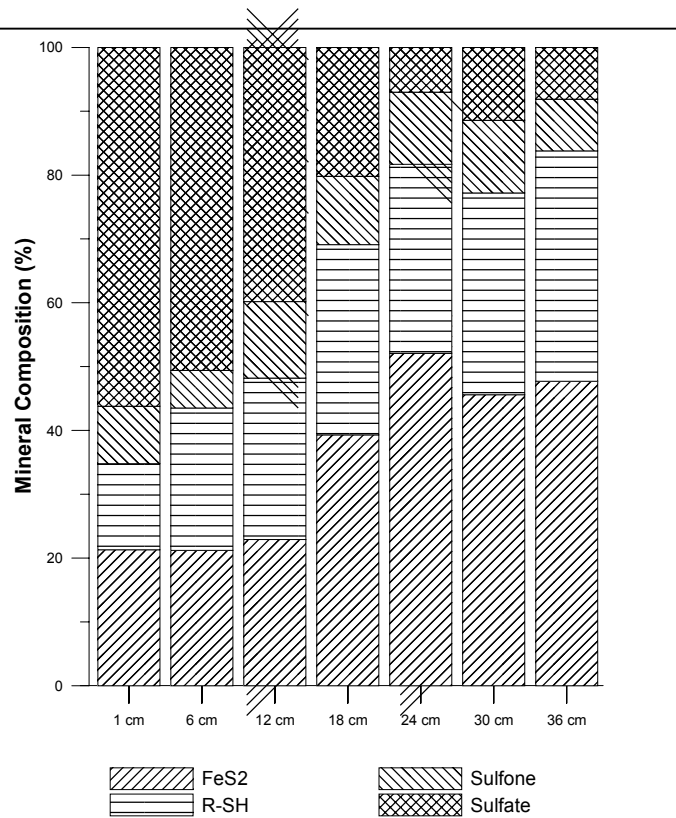


Figure 2: Peaceful Point XANES spectra analysis by sediment depth

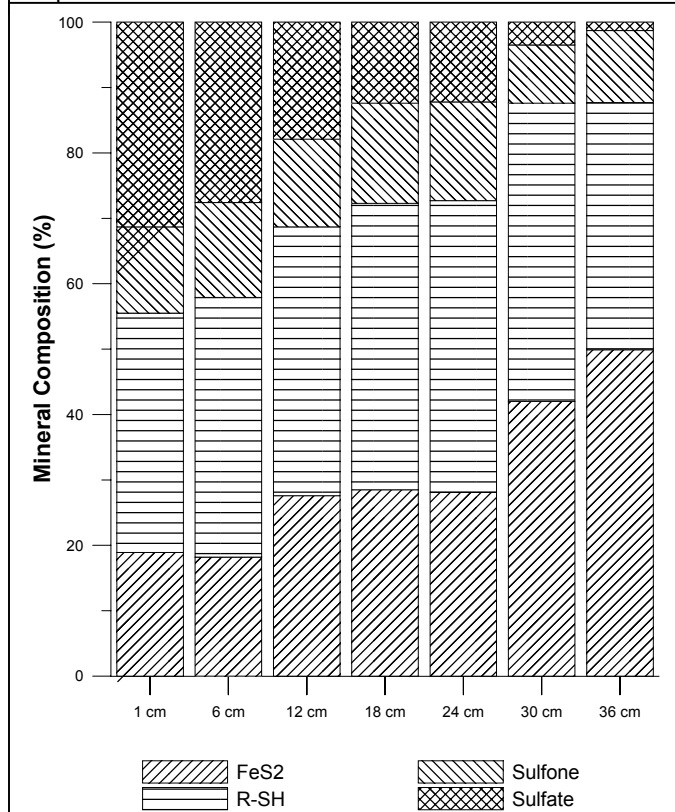


Figure 3: Harlow Point XANES spectra analysis by sediment depth

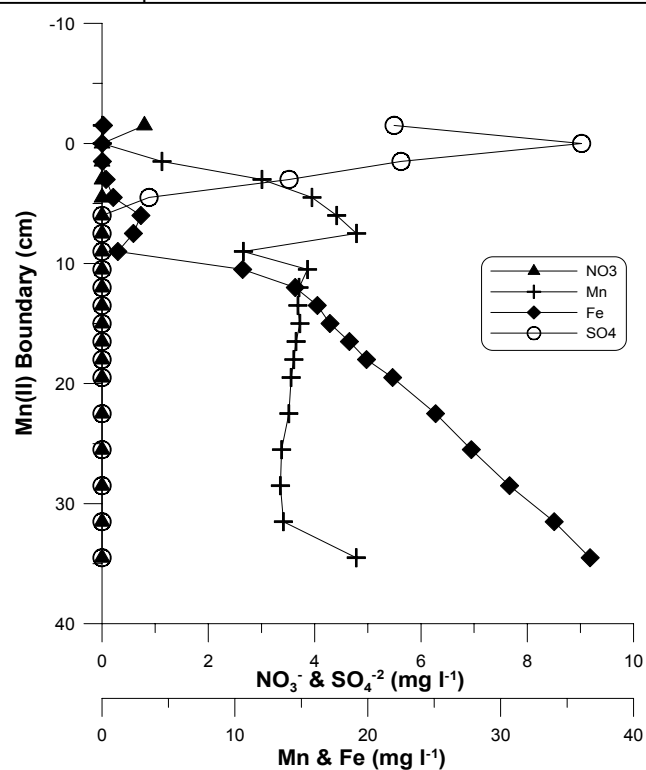


Figure 4: Pore water concentration of redox sensitive elements from Peaceful Point site, May 2003.